

PATENT SPECIFICATION

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(54) THERMOSETTING, FILM-FORMING SYNTHETIC RESIN COMPOSITION AND PROCESSES FOR THEIR PRODUCTION

(71) We, BASF FARBEN+FASERN AG, a German body corporate, of 2000 Hamburg, Am Neumarkt 30, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

10 The invention relates to thermosetting, film-forming synthetic resin compositions and to processes for their production. The resin compositions are, for example, suitable for stoving lacquers and, after neutralisation, as binders in water-based paints and for electrophoretic enamels.

15 Water-dilutable synthetic resins which contain adducts of polybutadiene and maleic anhydride together with unsaturated fatty acid esters are known from German Specification No. 2,016,233. Owing to the presence of fatty acid esters, however, the films obtained from these synthetic resins are not sufficiently stable to hydrolysis and yield insufficient gripping or throwing power values.

20 25 Likewise reaction products of polybutadiene with unsaturated fatty acid esters, maleic anhydride and polyisoprene resins are known from German Specification No. 2,411,350. These reaction products are also suitable for anodic deposition. However, relatively high stoving temperatures and longer stoving times for deposited resin films formed from the reaction products have to be accepted. Moreover, such reaction products on bright de-greased metal sheets in moist atmosphere show blister formation at 60°C.

30 35 The present invention seeks to overcome the known drawbacks of the state of the art and to prepare synthetic resin compositions of high corrosion resistance.

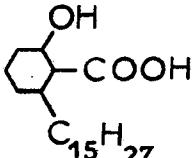
40 According to the present invention there is provided a thermosetting, film-forming synthetic resin composition containing the components:

- A. a phenol derivative having alkyl side chains, which contain at least one double bond; 45
- B. homopolymers of butadiene having average molecular weight between 300 and 6000 and iodine number between 200 and 600 or copolymers of butadiene with vinyl toluene; 50
- C. an α,β -ethylenically unsaturated carboxylic acid; 55
- D. formaldehyde

wherein either the reaction product of components B and C is reacted with a condensation product of components A and D or the reaction product of components A, B and C is reacted with component D to produce a condensation product. 60

The composition may contain additionally phenol as component E, wherein the reaction product of components B and C is reacted with the condensation product of components A, D and E. 65

The resin compositions according to the present invention contain free carboxyl groups and become water-dilutable through addition of ammonia, organic water-miscible amines or alkalis and may, in this form, be used as binders for aqueous thermosetting coating materials. In this form they are suitable for successful anodic deposition. Such resin compositions which are used for aqueous systems should, as a rule, possess acid numbers between 40 and 160. Outstanding values are obtained for gripping or throwing power, corrosion protection and stressing in damp heat atmospheres according to DIN (German Standard Specification) 500 17 in a damp heat chamber at 60°C. An electrodeposition bath including a resin composition according to the present invention is extremely stable and, after deposition and stoving at substantially lower temperatures and reduced stoving times, yields coatings with very good adhesion and with markedly good resistance to corro-

10	sion and outstanding resistance to water. The flexibility and hardness, the gloss and the pigment compatibility of the coatings so formed are excellent and they are substantially resistant to alkalis and acids. The corrosion examination in a salt spray test according to USA Standard ASTM B 117-64 gives higher values than was hitherto obtained from known resin compositions suitable for electrodeposition.	Treated or vacuum-distilled CNSL in which the anacardic acid is largely decarboxylated has, for example, the following chemical and physical properties:	50
15	As phenols with alkyl side chains which contain at least one double bond, suitable in particular are anacardic acid and Cardanol. The alkyl side chain of each of these two compounds ($-C_{15}H_{27}$) contains between 1 and 3 double bonds. Also suitable are diphenols, as for example, 3 - (8 - pentadecenyl)-, 3 - (8,11 - pentadecadienyl)-, 3 - (8,11,14 - pentadecatrienyl) - resorcinol. It has been found that the use of cashew nutshell liquid (hereinafter referred to as CNSL) gives excellent resin compositions with particularly advantageous properties.	Specific gravity at 25°C: 0.955 to 0.975 Viscosity at 25°C: 800 cP Acid number: 14 Iodine number: about 240 Ash: maximum 1% Moisture: maximum 0.5%	55
20	CNSL is a liquid obtained from the spongy intermediate layer between the kernel and the nutshell of Anacardium occidentale which contains about 90% of anacardic acid of the formula	In the present invention both untreated CNSL and vacuum distilled CNSL may be used either alone or in admixture.	60
25	30 and/or the decarboxylation product of anacardic acid, the so-called Cardanol of the formula	Particularly advantageous synthetic resin compositions with valuable technological properties are obtained with the use of cashew nutshell liquid.	65
30		As component B polybutadienes, in the form of the homopolymers of butadiene, and of average molecular weights between 300 and 6000 with iodine numbers between 200 and 600 are used.	70
35	and about 10% of diphenols, chiefly 3 - pentadecyl-, 3 - (8 - pentadecenyl)-, 3 - (8,11 - pentadecadienyl)- and 3 - (8,11,14 - pentadecatrienyl) - resorcinol.	By "polybutadienes" are to be understood all usual commercial isomers, both those with middle-positioned cis and trans double bonds and those with vinyl double bonds. Suitable, for example, are polybutadienes which have 65 to 75% of 1,4-cis, 25 to 35% of 1,4-trans and under 1% of 1,2-vinyl configurations. Also, polybutadienes which contain about 10% of 1,4-cis to 45% of 1,4-trans and up to 45% of 1,2-vinyl configurations. Fundamentally, all polybutadienes with molecular weight between 300 and 6000 may be used. Likewise, butadiene polymers such as are described in the journal "Rubber and Plastics Age", 1964, Vol. 45, No. 11, on page 1347, which contain terminal carboxyl groups, may be used.	75
40	CNSL is in common commercial use. Distinction is made between untreated CNSL which is obtained by cold pressing or by extraction and in this form contains up to 90% of anacardic acid. The physical and chemical properties of untreated CNSL are:	Also graft polymers of polybutadiene with 80% 1,4-cis and 20% 1,4-trans structure and a molecular weight of 1400 and an iodine number of about 350 with vinyl toluene are applicable.	80
45	Specific gravity at 26°C: 0.9668 to 1.0131 Refractive index at 41.5°C: 1.5158 Saponification value: 106 to 119 Acid number: 94 to 107 Iodine number: 270 to 296	As component C ethylenically unsaturated carboxylic acids are needed, by these are understood:	85
		α,β -ethylenically unsaturated monocarboxylic acids such as acrylic acid and methacrylic acid; α,β -ethylenically unsaturated dicarboxylic acids such as fumaric acid and maleic acid; anhydrides thereof such as maleic anhydride; half-esters of α,β -ethylenically unsaturated dicarboxylic acid with aliphatic alcohols with 1 to 6 carbon atoms. Suitable alcohols are methanol, ethanol, n-propanol, iso-propanol, butanols, amyl alcohols, n-hexanol.	90
		Various methods are used to prepare the thermosetting, film-forming synthetic resin compositions according to the present invention. One method is described with the following example:	95
		15-70 parts by weight of component B a polybutadiene with an average molecular	100
			105
			110

weight between 300 and 6000 and an iodine number between 250 and 600 and 65

30—85 parts by weight of component A a casew nutshell liquid is reacted by heating to 190° to 250°C for 30 to 180 minutes. The product obtained is then reacted with 70

5—25 parts by weight of component C an α,β -ethylenically unsaturated carboxylic acid at between 140°C and 200°C until 75

10 free carboxylic acids are no longer present. The received reaction product is then condensed with formaldehyde in the form of paraformaldehyde at between 40° and 100°C in the presence of alkaline catalysts. As a rule 80

15 2 to 5 hours are required. 85

As catalysts, either catalytic amounts of 90

20 tertiary amines, such as, triethylamine and tributylamine or sodium hydroxide or potassium hydroxide are used. The amounts used, 95

25 depending on the nature of the catalyst, lie between 0.01 and 0.3%. For the condensation reaction, preferably 3 to 8% by weight of paraformaldehyde is used. 100

The resin compositions obtained are as a rule diluted with water-soluble solvents which in part may also contain restrictedly water-soluble solvents or water-insoluble solvents. As such, suitable for example are ethanol, 105

25 propanol, isopropanol, ethyleneglycolmono-methyl, ethyl, isopropyl and butyl ethers as well as butanol, diethyleneglycol, monoethers and diethers of diethyleneglycol, methylethyl ketone, diacetone alcohol and dimethyl sulphoxide. Small proportions of water-insoluble 110

30 solvents such as for example xylene, benzene, cyclohexanone, nonanol and decanol may additionally be used. The total proportion of solvents should not exceed 20 to 30 parts by weight (with reference to 100 parts by weight of binder); the proportion of water-insoluble 115

35 solvents may be, as a maximum, 20 parts by weight of the amount of solvent used. 120

According to another process, ethylenically 125

40 unsaturated carboxylic acids (component C) are first reacted with the polybutadiene component B. This occurs for example as follows: 100 parts by weight of a polybutadiene with an average molecular weight between 300 and 6000 and an iodine number between 250 and 600 are reacted with 5 to 25 parts by weight of ethylenically unsaturated carboxylic acid at 140°C to 200°C, with stirring, in the presence of catalytic amounts of inhibitors. The amounts of inhibitors used are between 0.05 and 0.3 parts by weight. As inhibitors, suitable for example are hydroquinone, tertiary amylhydroquinone, diphenylamine, diphenylenediamine, copper or copper salts, e.g. copper naphthenate and others. The reaction has ended when free carboxylic acids or free carboxylic anhydride are no longer present. Normally, a time of between 2 and 5 hours is needed for the addition reaction. If an anhydride is used, the anhydride groups contained in the resultant adduct are subsequently opened by hydrolysis with water, possibly with the use of excess pressure in the presence of catalytic amounts of basic catalysts such as tertiary amines, e.g. triethylamine and tributylamine at 100 to 120°C in the course of about 1 to 3 hours. This reaction product (I) which is formed is subsequently dissolved in water-miscible organic solvents. The solids content should not be less than 70 per cent by weight. 30 to 85 parts by weight of Component A a CNSL, if necessary with

10 to 30 parts by weight of Component E are heated to 110 to 130°C and condensed with 10 to 30 parts by weight of Component D in the form of paraformaldehyde in the presence of hexamethylenetetramine (urotropine) and organic water-miscible solvents to give reaction product II. As a rule it suffices to heat Component A, a CNSL and where used Component E phenol to 110 to 130°C for 1 to 3 hours. The subsequent reaction with paraformaldehyde is effected as a rule at 70 to 80°C for 8 to 10 hours. The condensation reaction with the paraformaldehyde is preferably carried out in solution in organic water-miscible solvents with a solids content between 70 and 80 percent by weight. 0.5 to 2.5 parts of hexamethylenetetramine are used. The reaction product I obtained in the first step is mixed with the reaction product II in the ratio 1:3 to 4:1, with reference to the solids content. For this purpose, solutions of these reaction products I and II with in each case 70 to 80 per cent by weight solids content in organic water-miscible solvents are expediently used. The mixture is heated for 2 to 5 hours to temperatures between 50 and 100°C, preferably 55 to 75°C, and there is obtained as the end product a resin composition according to the invention as solution in organic solvents. The resin compositions according to the present invention become water-dilutable through addition of ammonia, organic amines and/or alkalis as neutralising agents. Suitable organic amines are for example dimethylamine, trimethylamine, triethylamine, diethylamine, propylamine, butylamine, mono-, di- and tri-ethanolamines, N-methylethanolamine, N,N-dimethylethanolamine and diisopropanolamines. Furthermore, sodium hydroxide, potassium hydroxide or lithium hydroxide may be used as alkalis. The aforesaid neutralising agents may be used individually or in admixture with one another. The resin compositions containing the neutralising agents are water-miscible. Depending on the nature and amount of the neutralising agent, aqueous solutions or dispersions of different degrees of viscosity are

5	obtained. These may be used as clear lacquers for baked or stoved coatings. The resin compositions may, however, also be pigmented with the usual pigments and contain fillers and customary lacquer auxiliaries and so form pigmented coating agents. The production of pigmented coating agents is effected in customary manner according to known methods in conventional devices such as dispersion apparatus, rolling mills, ball mills, sand mills, and dissolvers.	Parts mentioned are parts by weight; percentages are percentages by weight.	65
10	The resin compositions according to the presence invention are particularly suitable as binders for anodic deposition, in particular on metal surfaces.	Example 1.	
15	Resin compositions according to the present invention may, however, be used as binders for coating agents that are to be applied conventionally to surfaces that are to be coated by spraying, dipping and flow coating. The baking temperature of the coatings lies between 140°C to 160°C with baking times between 30 and 10 minutes.	540 g polybutadiene with a viscosity of 5 poises/20°C with about 80% cis and 20% trans structure and a molecular weight of about 1400 and an iodine number of about 350 was mixed with	70
20	The resin compositions according to the present invention give, after neutralisation, a clear lacquer which, after anodic deposition on untreated or zinc phosphated steel sheets and subsequent stoving for between 10 and 20 minutes at 140 to 160°C, forms a hard, tough-elastic, corrosion-resistant, condensed-moisture-resistant, acid- and alkali-resistant, glossy coating. The values for gripping or throwing power of water-diluted resin compositions according to the present invention in an electrophoresis bath are outstanding.	300 g CNSL, cold-pressed, with the following physical and chemical properties:	75
25	The bath is completely stable over very long periods of time and no deposits form. This clear lacquer may likewise contain customary pigments and additives which do not affect the good properties of the resultant electro-photically applied coating.	Specific gravity at 26°C: 0.9670 Saponification value: 109 Iodine number: 284 Acid number: 97 and, with stirring, heated to 220°C in about 15 minutes and kept at this temperature for 30 minutes.	80
30	The neutralised resin composition solutions may be used in pigmented form in customary manner with white and/or colouring pigments or fillers, white or coloured coatings being obtained which, after stoving at substantially 150°C, give, after 20 minutes, smooth, corrosion-resistant and high-gloss films on metal substrates, which films are exceptionally resistant to alkaline or acid agents. In the salt spray test according to ASTM B 117—64, values of more than 240 hours were found.	1.5 g copper naphthenate with 9% metal content and	85
35	To the resin compositions according to the invention there may be added small amounts of other compatible binders of different nature, for example, amino resins, phenolic resins, alkyd resins and maleic resins. The amounts of additional resins or binders used should not exceed 15%, with reference to the total weight of the synthetic resins according to the invention.	114 g maleic anhydride was added and heating to 220°C was subsequently effected. After about 2½ hours' duration of reaction, the content of free maleic anhydride had sunk to 0. The acid number of the adduct was about 95 mg KOH/g. The mixture was cooled to 100°C. Subsequently, 4 g triethylamine and	90
40	The following Examples are intended to illustrate the invention, without restricting it.	55 g paraformaldehyde was added and condensation was effected at 60°C for 4 hours. After addition of 110 g ethyleneglycolmonoethyl ether and 110 g isopropanol, a clear liquid product with the viscosity of 890 centipoises was obtained. The solids content was 81 per cent by weight.	95
45		Example 2.	
50		500 g polybutadiene with a viscosity of 9 poises/45°C and about 90% 1,2-vinyl and 10% 1,4-trans structure and a molecular weight of about 1200 and an iodine number of 420 was mixed with	105
55		250 g CNSL (distilled) with the physical and chemical properties:	110
60		Viscosity at 25°C: 800 cP Specific gravity at 25°C: 0.961 Iodine number: 240 Acid number: 12 Saponification value: 18 and, with stirring, heated to 230°C in about 15 minutes and kept at this temperature for 25 minutes. After cooling to 180°C, and after addition of 0.3 g diphenylparaphenylenediamine, reaction with	115
		140 g maleic anhydride was effected at 200°C. After 3 hours the content	120
			125

of free maleic anhydride had sunk to 0. The acid number of the adduct was 121 mg KOH/g. After cooling of the product to 100°C and addition of 5 3 g triethylamine, 48 g paraformaldehyde was added and condensation was effected at 60°C for 4 hours. Dilution was effected by 10 105 g ethyleneglycolmonobutyl ether and 105 g isopropanol. A clear viscous product with the viscosity of about 3000 centipoises with a solids content of about 80 per cent by weight was obtained.

Example 3.

400 g polybutadiene with a viscosity of 5 poises/20°C, 80% 1,4-cis and 20% 1,4-trans structure, a molecular weight of about 1400 and an iodine number of about 350 was heated to 150°C in an inert gas atmosphere. Within 2 hours a solution of 25 0.6 g tertiary butylperoxide in 60 g vinyltoluene was added uniformly and the temperature was kept at 150°C until a solids content of at least 95% was reached. The unreacted vinyltoluene was removed under vacuum. A graft polymer with a viscosity of 13 poises/20°C was obtained.

30 400 g of this graft polymer was mixed with 250 g CNSL — as in Example 1 — and, with stirring, heated to 220°C in about 15 minutes and kept at this temperature for 30 minutes. After cooling to 180°C, 40 0.2 g hydroquinone was added and heated with 95 g maleic anhydride to 200°C. After 3½ hours the content of free maleic anhydride had sunk to 0. The acid number of the adduct was 107 mg KOH/g. The same procedure was then followed as in Example 1. The product was diluted with ethyleneglycolmonoethyl ether and isopropanol in the ratio 1:1, to a solids content of 80 percent by weight. The viscosity was 5500 centipoises.

Example 4.

A. Production of component I:

55 650 g of a liquid polybutadiene with a viscosity of cP/50°C of 240, a density at 20 g of 0.8906, an iodine number of 449 and a molecular weight of 1800, which has 79% middle-positioned cis double bonds and 20% middle-positioned trans double bonds and 1% vinyl double bonds in the molecule structure, was heated at 100°C for 1 hour, with stirring and the passing through of nitrogen and with the addition of 0.25% of copper naphthenate. Thereafter, 65 88 g maleic anhydride was added. With stirring and the passing over of nitrogen, the temperature was increased to 200°C. After a reaction duration of 15 minutes, the initially heterogeneous mixture changed into a clear homogeneous solution. After a reaction duration of 3 hours at 200°C the content of maleic anhydride had sunk to 0. The mixture was subsequently cooled to 80°C and, after addition of 80 5 g triethylamine and 20 g water, kept at 120°C for 2 hours. The anhydride ring contained in the adduct was split open. Subsequently, dilution was effected with ethyleneglycolmonoethyl ether and isopropanol in the ratio of 1:1 until there was a solids content of 80 per cent by weight.

B. Production of Component II:

In a reaction vessel 500 parts of CNSL (distilled) with the following physical and chemical properties:

Specific gravity at 25°C: 0.950
Viscosity at 25°C in centipoises: 95 730
Iodine number: 235
Acid number: 12
Saponification value: 16
was mixed with 150 parts phenol and 100 heated to 120°C for 2 hours. Subsequently, the product was cooled to 80°C and dissolved in ethyleneglycolmonoethyl ether until there was a solids content of 80 per cent by weight. After addition of 105 25 parts hexamethylenetetramine and 140 parts paraformaldehyde, 110 stirring was effected for 16 hours at 75°C.

C. 60 parts of the above component I and 40 parts of the above component II were combined and treated for 4 hours at a temperature of 65°C.

Example 5.

Component I, an adduct of a polybutadiene with maleic anhydride, was formed as in A of Example 4 using a polybutadiene with an average molecular weight of 1000, an iodine number of 357 and a content of 120 45 per cent by weight of vinyl groups, 45 per cent by weight trans content and 10 per cent by weight cis content. For 500 g of this polybutadiene, 84 g of maleic anhydride were

used. The product obtained was diluted with ethyleneglycolmonoethyl ether and isopropanol in a ratio of 1:1 until there was a solids content of 80%.

5 The production of component II was effected analogously to Example 4.

70 parts of the above component I and 30 parts of the component II were combined and kept at 70°C for 4½ hours stirring.

10 Example 6.

The resin compositions obtained according to Examples 1 to 5 were neutralised with

1. Ammonia;
2. Dimethylethanolamine;
3. Potassium hydroxide and dimethylethanolamine;
4. Trimethylamine plus dimethylethanolamine 1:2;
5. Sodium hydroxide and triethanolamine in the ratio 1:4.

20 The amount of neutralising agent was such that a 10% strength aqueous solution had a pH value between 6.5 and 8.

25 The resulting binders were clear, oily, medium to highly viscous liquids which could be stored indefinitely.

With these binders the following experiments were carried out:

Example 7.

A coloured paste was obtained by adding to the binders of Example 6 red iron oxide in the ratio of 1:1. On dilution with water (and possibly with the addition of small proportions of water-miscible solvents) to adjust the viscosity, coating agents were obtained that could be applied by dipping, flow coating or spraying techniques. These coating agents had a solids content between 30 and 45 per cent by weight. The films or coatings formed from the coating agents were stoved at 140°C for 20 minutes or at 200°C for 3 minutes and even on iron sheet that has not been pretreated, hard elastic films or coatings with outstanding corrosion resistance to salt spray, industrial atmospheres, moisture and acids and alkalis were obtained. The mechanical properties of the films or coatings were clearly superior to known films or coatings.

30 35 40 45 50 Table I summarises the measured values for a salt spray test.

TABLE I

Example	Neutralising agent according to Example 6	Solids content in %	Layer thickness (microns)	Pretreatment of the metal sheet	Salt spray test ASTM B 117-64 hours
1	1	25	14	phosphatised	>240
1	2	25	16	untreated (degreased)	>240
2	4	30	22	untreated (degreased)	>240
2	2	20	16	untreated (degreased)	>240
3	1	25	16	untreated (degreased)	>240
4	1	25	18	phosphatised	>240
5	2	30	15	untreated	>240
5	4	20	20	untreated	>240

Example 8.

55 290 g of the synthetic resin according to Example 1 neutralised with ammonia was ground with

20 g titanium dioxide, 20 g red iron oxide, and 20 g aluminium silicate on a three-roller mill. The pigment paste was 60

5	diluted with 1600 g of de-ionised water and adjusted to a pH value of 7.5 by further addition of ammonia.	dipcoating bath was obtained which, after adjustment to a pH value of 7.3, is used as stated in Example 8.	35
5	In a metal vessel of 2.5 litres capacity which was connected to form a cathode, a dense, readily washable film or coating was deposited at 25°C in one minute at 200 to 300 volts direct current on to a 200 cm ² anode consisting of phosphatised steel sheet.	The coatings obtained had a layer thickness of about 28 microns. After test duration of 240 hours in the salt spray test, a metal sheet undergoing the test showed no visible changes of any kind.	35
10	After hardening at 20 minutes at 130°C a smooth, pore-free coating of 25 microns thickness was formed.	If the electro-dipcoating bath was stirred for 200 hours at 40°C, there was likewise obtained from this aged mixture flawless, unchanged coatings with unchangedly good corrosion protection.	40
15	After 240 hours of a salt spray test according to ASTM, the steel sheet showed no change of any kind.	The examination of stressing in damp heat atmospheres is effected according to DIN (German Standard Specification) 50017 SK (60°C). By this test is found how long a time coatings may be exposed to extreme moisture effects without lacquer troubles occurring.	45
20	The electro-dipcoating bath was stirred for 200 hours at 40°C and then cooled to 25°C. Thereafter, the deposition described above was repeated. There was obtained in the same manner a defect-free coating and the same values in the salt spray test were obtained.	In Table II are summarised the individual values for the salt spray test in the case of anodic deposition and for the stressing in the damp heat atmospheres according to DIN 50017 SK (60°C).	50
25	Example 9. 330 g of the un-neutralised synthetic resin composition according to Example 4 were ground with	The testing of the resistance to the influence of acids and alkali was investigated on stoved coating films on phosphatised steel sheet. It was found that in the case of 48 hours' storage in alkalis and acids of different strength excellent values were obtained.	55
30	32 g titanium dioxide, 32 g aluminium silicate and 2 g carbon black on a rolling mill. After addition of 10% strength potassium hydroxide solution and 1600 g of demineralised water, an electro-	60	

TABLE II

Example	pH value	Deposition voltage/ deposition time	Layer thickness after stoving (microns)	Salt spray test according to ASTM B 117-64 hours	Test according to DIN 50017 SK (60°C) without change after	Remarks
8	6.5	250 volts/1 min.	18	>240	120h	
8	7.1	200 volts/2 min.	21	>240	120h	
8	6.5	200 volts/2 min.	20	>240	120h	
8	6.8	250 volts/1 min.	21	>240	120h	
8	7.0	180 volts/2 min.	21	>240	120h	
9	7.4	150 volts/2 min.	23	>240	120h	
9	7.1	130 volts/2 min.	19	>240	120h	
9	6.9	150 volts/2 min.	21	>240	120h	
9	6.7	150 volts/3 min.	24	>240	120h	
9	6.4	130 volts/3 min.	20	>240	120h	

WHAT WE CLAIM IS:—

1. A thermosetting, film forming synthetic resin composition containing the components:
 - 5 A. a phenol derivative having alkyl side chains, which contain at least one double bond;
 - B. homopolymers of butadiene having average molecular weight between 300 and 6000 and iodine number between 200 and 600 or copolymers of butadiene with vinyl toluene;
 - C. an α,β -ethylenically unsaturated carboxylic acid;
- D. formaldehyde wherein either the reaction product of components B and C is reacted with a condensation product of components A and D or the reaction product of components A, B and C is reacted with component D to produce a condensation product.
2. A composition as claimed in claim 1 containing additionally phenol as component E, wherein the reaction product of components B and C is reacted with the condensation product of components A, D and E.
3. A composition as claimed in claim 1 or

D. formaldehyde

wherein either the reaction product of components B and C is reacted with a condensation product of components A and D or the reaction product of components A, B and C is reacted with component D to produce a condensation product.

15 2. A composition as claimed in claim 1 containing additionally phenol as component E, wherein the reaction product of components B and C is reacted with the condensation product of components A, D and E.

20 3. A composition as claimed in claim 1 or

2, in which said component A is derived from cashew nutshell liquid.

4. A composition as claimed in claim 3, in which the cashew nutshell liquid is untreated cashew nutshell liquid obtained by cold pressing the spongy intermediate layer between the kernel and the nutshell of *Anacardium occidentale*.

5. A composition as claimed in claim 3, in which the cashew nutshell liquid is vacuum-distilled cashew nutshell liquid.

6. A composition as claimed in claim 3, in which the cashew nutshell liquid is a mixture of untreated and/or vacuum-distilled cashew nutshell liquid.

7. A composition as claimed in any preceding claim in which the said component A is one or more of anacardic acid, Cardanol, 3 - (8 - pentadecenyl)-, 3 - (8,11 - pentadecadienyl)-, 3 - (8,11,14 - pentadecatrienyl) - resorcinol.

8. A composition as claimed in any preceding claim in which said component C is a α,β -ethylenically unsaturated dicarboxylic acid, an anhydride thereof and/or an half-ester of the α,β -ethylenically unsaturated dicarboxylic acid with an aliphatic alcohol with 1 to 6 carbon atoms.

9. A composition as claimed in claim 8 wherein said component C is maleic acid, maleic anhydride or fumaric acid.

10. A composition as claimed in any preceding claim in which said component B is a graft polymer of a polybutadiene consisting of 80% 1,4-cis and 20% 1,4-trans structure, having a molecular weight of about 1400 and an iodine number of about 350 with vinyl-toluene.

11. A composition as claimed in any preceding claim obtained by reaction of component D with a reaction product of:

component A:

30—85 parts weight cashew nutshell liquid;

component B:

45 15—70 parts by weight polybutadiene with an average molecular weight of between 300 and 6000 and an iodine number between 250 and 600;

component C:

50 5—25 parts by weight α,β -ethylenically unsaturated monocarboxylic acid and/or α,β -ethylenically unsaturated dicarboxylic acid and/or anhydride thereof and/or half ester of α,β -ethylenically unsaturated dicarboxylic acids with an aliphatic alcohol with 1 to 6 carbon atoms.

55 12. A composition as claimed in claim 2 obtained by reaction of a reaction product (I) of:

60 component B:

100 parts by weight polybutadiene with an average molecular weight of between 300 and 6000 and an iodine number between 250 and 600;

component C:

65 5—25 parts by weight α,β -ethylenically unsaturated monocarboxylic acid and/or α,β -ethylenically unsaturated dicarboxylic acid and/or anhydride thereof and/or half ester of α,β -ethylenically unsaturated dicarboxylic acids with an aliphatic alcohol with 1—6 carbon atoms

70 with a reaction product (II) of

component A:

75 30—85 parts by weight cashew nutshell liquid

component D:

80 10—30 parts by weight formaldehyde, if necessary

component D:

85 10—30 parts by weight phenol, the ratio of I to II being as 1:1 to 4:1.

13. A composition obtained by neutralising a composition as claimed in any preceding claim with ammonia, organic water-miscible amines and/or alkali.

14. A composition as claimed in any of the preceding claims in association with a water-soluble solvent, which in part may also contain restrictedly water-soluble solvents or water-insoluble solvents.

15. An unpigmented stoving lacquer or a stoving lacquer containing pigments and/or fillers including as binder a composition as claimed in any preceding claim.

16. A water-dilutable stoving lacquer including a composition as claimed in claim 13 neutralised with ammonia, organic water-miscible amines and/or alkali.

17. An electrodeposition lacquer for anodic deposition including a composition as claimed in any of claims 1 to 14.

18. A lacquer as claimed in claim 17 in which the composition has an acid number between 40 and 160.

19. A lacquer as claimed in any of claims 15 to 18 in which the composition is contained in combination with not more than 15% by weight of other binders, related to the weight of said composition.

20. A lacquer as claimed in claim 19 in which the other binders are amino resins, phenolic resins, alkyd resins or maleic resins.

21. Thermosetting, film-forming synthetic resin composition as herein described with reference to the Examples.

22. A process for the production of a thermosetting, film-forming synthetic resin composition substantially as herein described.

23. A coating process wherein metallic or other conductive objects are coated by a process of electrodeposition with a water-soluble

resin composition as claimed in the claims
17 to 20.

24. A coated object wherein at least part
of the coating is deposited by a process as
5 claimed in claim 23.

J. MILLER & CO.,
Chartered Patent Agents,
Agents for the Applicants,
Lincoln House,
296-302 High Holborn,
London C1V 7JH.

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